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$$\begin{aligned} X &= vr - wq, \quad Y = wp - ur, \quad Z = uq - vp, \\ P &= u_1 X + w' Y + v' Z, \\ Q &= w' X + v_1 Y + u' Z \\ R &= v' X + u' Y + w_1 Z, \end{aligned}$$

and w_2 is a numerical factor.

Each of these equations is of the degree $18u - 36$ in the variables; but it is shown in the paper that they are all divisible by H , and that they further differ only in respect of the several factors u^3, v^3, w^3 . Dividing these out, the degree of the result is reduced to

$$(18n - 36) - 3(n - 2) - 3(n - 1) = 12n - 27,$$

as it should be. I have not thought it necessary to reduce the expressions completely, as the form of the result given by Professor Cayley leaves nothing to be desired, and the point specially considered here is the degree of the equation. At the same time, the reductions necessarily effected in the course of the proof of the extraneous factors are sufficient to indicate that the formulæ of the present memoir would lead to an equation of the same form as that given by Professor Cayley.

XI. "Products of the Destructive Distillation of the Sulphobenzolates. No. I." By JOHN STENHOUSE, LL.D., F.R.S., &c. Received June 14, 1865.

Preparation of Sulphobenzolic Acid. Purification of the Benzol.

As most specimens of benzol met with in commerce, even when rectified, contain impurities besides toluol and the other homologues of benzol, I have generally found it necessary to submit it to purification before using it for the preparation of sulphobenzolic acid. The commercial article boiling between 80° and 90° C., was mixed with about one-twentieth of its bulk of concentrated sulphuric acid, and digested for eight or ten hours in a flask furnished with a long condensing-tube. By this means a considerable amount of the impurities contained in the crude benzol were converted by the acid into a black gelatinous mass similar in appearance to that obtained in the preparation of olefiant gas, a large quantity of sulphurous acid gas was given off, and the impure benzol acquired a reddish-brown or dark purple colour. It was separated from the black mass, washed with a small quantity of water, and again heated once or twice with concentrated acid, but for a shorter time than at first, until fresh acid when heated with it ceased to become dark-coloured. In this operation the benzol loses from 10 to 20 per cent., according to the amount of impurity present, and small quantities of sulphobenzolic acid are produced.

Conversion of Benzol into crude Sulphobenzolic Acid.

This acid may be prepared by the process given by Mitscherlich, which consists in adding benzol to fuming oil of vitriol contained in a flask, as long as it dissolves, with agitation and frequent cooling. Notwithstanding

Mitscherlich's statement* that he has "succeeded as little as Faraday in combining benzol with ordinary strong sulphuric acid," I have found it advisable, when large quantities of sulphobenzolic acid are required, to treat the purified benzol with ordinary commercial acid.

Concentrated sulphuric acid and purified benzol, in the proportion of about four measures of the former to five of the latter, were placed together in a flask furnished with a long condensing-tube, and heated on a sand-bath for eight or ten hours. The flask in which the digestion is performed should be very large in proportion to the quantity of benzol employed, so that an extensive surface is exposed to the action of the acid†.

Sulphobenzolates.

The crude sulphobenzolic acid obtained by either of the above methods was separated from the uncombined benzol, and a quantity of water, about twenty times the bulk of the sulphuric acid originally employed, was added to it. This solution, which has a small quantity of sulphobenzene, $C_{12}H_{10}SO_2$, suspended in it, was heated to the boiling-point, neutralized with chalk, diluted with ten parts more water, and after being boiled for a few minutes, was filtered from the sulphate of calcium. The clear and slightly coloured filtrate is a solution of *sulphobenzolate of calcium*, $CaC_6H_5SO_3$, from which the salt may be obtained by sufficient concentration. *Sulphobenzolate of barium* may likewise be prepared in a similar manner to the calcium salt, substituting carbonate of barium for chalk. The *sulphobenzolates of the alkaline metals* are readily obtained by precipitating the solution of the calcium salt by the carbonate of the desired metal, and evaporating the solution. By this process purified benzol yielded nearly twice its weight of sulphobenzolate of sodium. The *sulphobenzolates of copper, zinc, &c.*, are best prepared by precipitating the solution of the barium compound by solutions of their sulphate. The copper salt is usually described in handbooks, on Mitscherlich's authority‡, as forming fine large crystals. I have only been able to obtain it, whether from water or spirit, in very small crystals, which are exceedingly soluble.

Decomposition of Sulphobenzolate of Sodium.

The sodium-salt, after being reduced to powder and thoroughly dried, was introduced into a copper flask furnished with a bent tube, and submitted to destructive distillation, when an oily body covered with a layer of water condensed in the receiver, and a considerable quantity of carbonic and some sulphurous acid gas were evolved, carbonaceous matter and carbonate of sodium remaining in the retort. In order that the operation may proceed rapidly, and in the most advantageous manner, the quantity of sub-

* Pogg. xxxi. p. 284.

† A similar process has been employed by Gerhardt and Chancel in the preparation of sulphite of chlorobenzene, Compt. Rend. vol. xxxv. p. 690.

‡ Gmelin's Handbook, vol. xi. p. 156; Gerhardt, vol. iii. p. 72.

stance introduced into the retort should not exceed 25 to 30 grammes at each distillation.

Florence flasks can be used; but, owing to their bad conducting-power and the high boiling-point of the oil, the result is not so favourable. When the distillation is properly conducted in a copper retort, the dried sodium-salt yields from one-fourth to one-fifth of its weight of crude oil.

The crude oil was separated from the supernatant layer of water, and distilled in a retort furnished with a thermometer. It began to boil at 80°C ., and then rose slowly to 110°C ., the distillate between these temperatures consisting of a small quantity of water and benzol. When the water had all passed over, the boiling-point rose very rapidly to 290°C ., at which temperature the greater portion of the liquid distilled over, leaving a black tarry residue in the retort. This black residue, when more strongly heated, gave a further quantity of an oily body, which, when rectified, first yielded the substance boiling at about 290°C ., and above 300°C . a liquid which on standing some weeks deposited a small quantity of crystals. The quantity boiling between 290° and 300°C . was about two-thirds the weight of the crude oil.

The rectified oil between 290° and 300°C . was again distilled, when nearly the whole of it came over at $292^{\circ}\cdot 5\text{C}$., the boiling-point being remarkably constant. After another rectification in a current of hydrogen, it was subjected to analysis—the carbon and hydrogen being determined by combustion with oxide of copper and a current of oxygen, and the sulphur by ignition with carbonate of sodium and oxide of mercury.

I. .603 grm. oil gave 1.708 grm. CO_2 and .292 grm. H_2O .

II. .595 grm. oil gave 1.679 grm. CO_2 and .288 grm. H_2O .

III. .237 grm. oil gave .302 grm. sulphate of barium.

IV. .275 grm. oil gave .354 grm. sulphate of barium.

	Theory.	I.	II.	III.	IV.	Mean.
$\text{C}_{12}=144$	77.41	77.25	76.98	77.12
$\text{H}_{10}=10$	5.38	5.38	5.38	5.38
$\text{S}=32$	17.20	17.48	17.51	17.49
	186	99.99				

The formula $\text{C}_{12}\text{H}_{10}\text{S}$, deducible from these analyses, is that of sulphide of phenyl, or a body isomeric with it. When pure it is nearly colourless, having only a very faint yellow tinge, and an aromatic but slightly alliacious odour. It has a high refractive power, sp. gr. 1.119, and boils at $292^{\circ}\cdot 5$. It is insoluble in water, very soluble in hot spirit, from which it partially separates on cooling, and is miscible in all proportions with ether, bisulphide of carbon, and benzol. Its alcoholic solution, when mixed with bichloride of platinum, gives a slight flocculent precipitate, which on standing resolves itself into a reddish-coloured oil. Nitrate of silver and chloride of mercury give no precipitate.

When the oil was treated with sulphuric acid, it dissolved in small quan-

tity, forming a red solution, which, on the application of a gentle heat, changed to a fine purple colour; this disappeared on raising the temperature, the whole of the oil dissolved, and a solution was obtained of a faint greenish-black tinge. When this solution was largely diluted with water it became nearly colourless, and on neutralization with chalk yielded (besides the sulphate) an organic calcium-salt, very soluble in water. The solution of the oil in sulphuric acid, when very strongly heated, blackened and gave off sulphurous acid gas. Solutions of the alkalis, whether aqueous or alcoholic, appear to have no action on the oil; but when heated with solid potash, it was decomposed with the production of compounds I am at present investigating.

Action of oxidizing Agents on Sulphide of Phenyl.—*Sulphobenzolene.*—When the oil $C_{12}H_{10}S$ was brought into contact with strong nitric acid, a very violent action ensued, accompanied by the copious evolution of nitrous fumes. The mixture was then boiled for an hour or two with occasional addition of fresh nitric acid, and the solution thus obtained poured into a large quantity of water, when a crystalline mass of a pale yellow colour was precipitated. This, when perfectly dried, was reduced to powder and washed with ether to remove a small quantity of adhering oil, and the partially purified product was recrystallized once or twice from benzol, and then several times from spirit, collecting apart the first portions which separate. By this means a substance in beautiful oblique prismatic crystals was obtained in a state of perfect purity, whilst in the mother-liquors there remained a large quantity of the same body mixed with a second substance crystallizing in long needles, which, however, formed but an inconsiderable portion of the whole.

Although this is the method by which I first prepared the above described substance crystallizing in oblique prisms, I have since employed a process which yields it with greater facility and in a much purer state. Ten parts by weight of water, five of concentrated sulphuric acid, and two of sulphide of phenyl, were placed in a flask furnished with a long condensing-tube, and to the mixture, kept boiling, three parts of acid chromate of potassium were added in small portions at a time. The digestion continued for twenty or thirty minutes, and the mixture was then allowed to cool. The green liquid was poured off from the cake of crystals, which, after boiling with water to free it from sulphuric acid, was dried. The nearly pure substance was then crystallized, once from benzol and once from alcohol, when it formed brilliant crystals which were perfectly pure. A trace of the second substance previously mentioned, crystallizing in long needles, was found in the benzol mother-liquors. By this last process, which is greatly preferable to the nitric acid one, the rectified oil yielded its own weight of crystals.

I. .338 grm. crystals gave .820 grm. CO_2 and .144 grm. H_2O .

II. .346 grm. crystals gave .834 grm. CO_2 and .144 grm. H_2O .

III. .349 grm. crystals gave .844 grm. CO_2 and .156 grm. H_2O .

IV. .241 grm. crystals gave .259 grm. sulphate of barium.

V. .362 grm. crystals gave .385 grm. sulphate of barium.

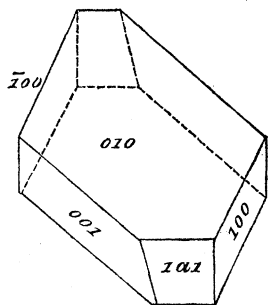
VI. .270 grm. crystals gave .293 grm. sulphate of barium.

	Theory.	I.	II.	III.	IV.	V.	VI.
$\text{C}_{12}=144$	66.06	66.18	65.75	65.97
$\text{H}_{10}=10$	4.59	4.73	4.62	4.96
$\text{S}=32$	14.68	14.74	14.59	14.89
$\text{O}_3=32$	14.68
	218	100.01					

This substance was analyzed in the same manner as the sulphide of phenyl,—Nos. III., IV., V. being prepared by the nitric acid process, and Nos. I., II., VI. by oxidation with acid chromate of potassium and sulphuric acid.

The analysis of this substance leads to the formula $\text{C}_{12}\text{H}_{10}\text{SO}_2$, which is the same as that of the sulphobenzene of Mitscherlich. It differs greatly from that body, however, both in its chemical and physical properties. I shall therefore provisionally call it sulphobenzolene.

It forms oblique prisms, which are often of large size when prepared by crystallization out of benzol, in which it is rather soluble. The crystals obtained by both the processes above described were kindly measured for me by my friend Charles Brooke, Esq., F.R.S., who states they “are of the same form, the measurements corresponding exactly. They belong to the oblique prismatic system. The measurements must be considered as only approximative, the surfaces of the crystals being imperfect.” No planes have been observed to determine the symbol a of the plane $1a1$.



010 on 001 or 100.....	$94 \frac{30}{100}$
010	$\bar{1}00$ $85 \frac{30}{100}$
010	$1a1$ $108 \frac{20}{100}$
001	$\bar{1}00$ $110 \frac{20}{100}$

It is very soluble in hot spirit, from which it separates on cooling in a manner closely resembling the crystallization of chlorate of potassium. It is also soluble in ether, bisulphide of carbon, and slightly in boiling water, crystallizing out completely on cooling. It melts at 126°C ., and distils at a much higher temperature.

Sulphobenzolene dissolves readily in concentrated sulphuric acid, and is not decomposed even when the solution is heated to the boiling-point.

Water precipitates the substance unchanged. Aqueous solutions of the alkalies appear to have no action on the crystals; but when they are heated with solid potash a powerful reaction takes place, with the production of new compounds.

When sulphobenzolene is digested for some time with a mixture of concentrated nitric and sulphuric acids, it dissolves, and red fumes are evolved. If a large quantity of water be now added to the mixture, a copious precipitate is obtained, difficultly soluble in hot alcohol, from which it crystallizes in minute needles.

Decomposition of Sulphobenzolate of Calcium.

When this salt was distilled in the manner described for the sodium compound, it underwent a similar decomposition—water and oil collecting in the receiver, and carbonic and sulphurous acids being evolved. In this instance, however, a very high temperature was required, and the quantity of oil obtained was much smaller than from the sodium-salt, being only about one-sixteenth the weight of the dry sulphobenzolate of calcium employed. The crude oil, when rectified, commenced to boil at 80°C. , between which and 110°C. small quantities of water and benzol came over. The boiling-point then rose rapidly to 280°C. , between which temperature and 300°C. about one-fifth of the original quantity of oil came over. Above 300°C. the distillate obtained became almost solid on cooling, consisting apparently of the same crystalline body of which a small quantity only was obtained in the rectification of the crude oil from the sodium-salt.

The portion distilling between 280° and 300°C. , when submitted to the action of sulphuric acid and acid chromate of potassium, yielded a crystalline cake, which, after washing, was dissolved in hot benzol; on cooling, a few oblique prismatic crystals of sulphobenzolene were obtained, and likewise a large quantity of the needle-formed crystals, probably held dissolved in the oil previously to its being oxidized. These I am at present examining.

Decomposition of Sulphobenzolate of Ammonium.

This salt, which melts at about 200°C. , is decomposed with great facility, and at a comparatively low temperature, yielding large quantities of bisulphite of ammonium and benzol, with some undecomposed sulphobenzolate of ammonium, and likewise a very small quantity of a crystalline substance slightly soluble in cold water, the only residue in the retort being a little carbonaceous matter. On rectifying the benzol obtained in this decomposition, a small quantity of a heavy oil was obtained, having a high boiling-point, and which deposited crystals on cooling. When oxidized, sulphobenzolene seems to be formed in small quantity.

Sulphobenzolamide.

The crystalline substance which occurs in small quantity, amounting to about one and a half per cent., among the products of the destructive dis-

tillation of sulphobenzolate of ammonium, is washed with cold water to free it from the ammonium salts with which it is accompanied, dissolved in boiling water, and filtered to separate it from adhering traces of oil. On the cooling of this solution, the impure sulphobenzolamide is deposited in large micaceous scales. By one or two crystallizations out of spirit, and one from boiling water, it is obtained perfectly pure and white.

- I. .350 grm. gave .590 grm. CO_2 and .144 grm. H_2O .
- II. .442 grm. gave .740 grm. CO_2 and .182 grm. H_2O .
- III. .343 grm. gave .219 grm. platinum.
- IV. .237 grm. gave .148 grm. platinum.
- V. .252 grm. gave .376 grm. sulphate of barium.
- VI. .432 grm. gave .645 grm. sulphate of barium.
- VII. .124 grm. gave .186 grm. sulphate of barium.

	Theory.	I.	II.	III.	IV.	V.	VI.	VII.	Mean.
$\text{C}_6=72$	45.85	45.98	45.66	45.82
$\text{H}_7=7$	4.46	4.57	4.57	4.57
$\text{N}=14$	8.92	9.03	8.84	8.93
$\text{S}=32$	20.38	20.46	20.48	20.58	20.51
$\text{O}_2=32$	20.38	20.17
	157	99.99							100.00

These analyses correspond to the formula $\text{C}_6\text{H}_7\text{NSO}_2$, which is that of sulphobenzolamide, equivalent to sulphobenzolate of ammonium minus one atom of water, $\left. \begin{matrix} \text{C}_6\text{H}_5 \\ \text{NH}_4 \end{matrix} \right\} \text{SO}_3 - \text{H}_2\text{O} = \text{C}_6\text{H}_7\text{NSO}_2$.

Sulphobenzolamide crystallizes in large and very lustrous micaceous scales, greatly resembling naphthalin in appearance. It fuses at 153°C ., and recrystallizes on cooling; when more highly heated, it volatilizes. It is extremely difficult to reduce the dry crystals to powder, owing to their toughness. When boiled with a strong solution of potash it gives off ammonia, sulphobenzolate of potassium being apparently formed at the same time. Weak acids have little or no action on it. The analyses were made for me by my assistant, Mr. C. E. Groves.

XII. "An Account of the Base-observations made at Kew Observatory with the Pendulums to be used in the Indian Trigonometrical Survey." By BALFOUR STEWART, F.R.S., and B. LOEWY, Esq. Received June 15, 1865.

[This Paper will be published in a subsequent Number.]